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Abstract

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ON THE MOLECULAR REFRACTIONS OF BORON-NITROGEN COMPOUNDS

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The application of Lorentz-Lorenz molecular refractions (MR) to the study of organic boron compounds has been investigated for a comparatively long time. To determine the calculated (“theoretical”) value of MR, certain values of the refractions of the bond of boron with various elements have been published; among them the most complete are the data of Mikhailov ([1]) and Seri ([2]).

It is known that, in the general case, each compound corresponds to its own value of the molecular refraction. Comparison of MR_{exp} with MR_{calc} makes it possible to draw certain (although most often preliminary) conclusions regarding the structure of the compound under investigation, provided that: 1) if the difference $|\Delta| = MR_{\text{exp}} - MR_{\text{calc}}$ is too large, the assumption that the compound has the given structure is rejected, or a check of the initial values n_D^t and ρ_4^t is necessary; 2) if the difference $|\Delta|$ is small, the hypothesis is accepted.

In the present work an attempt is made to show the possibility of a mathematical approach to solving the problem, and to give objective criteria for the correct evaluation of the magnitude $|\Delta|$.

First of all, it is necessary to know with what accuracy the value

$$MR_{\text{calc}} = \overline{MR} \pm \varepsilon, \tag{I}$$

has been determined, where $\overline{MR}$ is the most probable value of the calculated value of the molecular refraction; ε is a quantity characterizing the confidence limits of the calculated value of the molecular refraction.

Expression (I) shows that the value MR_{calc} may, generally speaking, take any values from $(\overline{MR} - \varepsilon)$ to $(\overline{MR} + \varepsilon)$.

If now, upon comparison, it turns out that

$$\overline{MR} - \varepsilon < MR_{\text{exp}} < \overline{MR} + \varepsilon, \tag{II}$$

then the hypothesis concerning the possible structure of the substance is accepted.

If, however,

$$MR_{\text{exp}} > \overline{MR} + \varepsilon \tag{III}$$

or

$$MR_{\text{exp}} < \overline{MR} - \varepsilon, \tag{IIIa}$$

then the hypothesis is rejected.

In the case when the structure of the substance is known, and there are no gross deviations in the determination of n_D^t and ρ_4^t, the occurrence of inequality (III) or (IIIa) indicates the presence of specific features in the structure of the compound.

Thus, the problem of comparing MR_{exp} and MR_{calc} loses its subjective character, since it becomes clear which deviations are due to measurement errors within the framework of the accepted additivity scheme, and which are due to features of the structure of the compound.

To determine the value ε in expression (I), one may use the methods of mathematical statistics, assuming a priori that the errors in

determinations of bond refractions are random in character and are normally distributed ([3,4]).

It is easy to show that, since MR is a linear function of m variables, the quantity

$$\overline{MR} = k_1\overline{R}_1 + k_2\overline{R}_2 + \dots + k_m\overline{R}_m = \sum_{i=1}^{m} k_i R_i, \tag{IV}$$

and the standard error of the quantity $\overline{MR}$ is equal to:

$$S_{\overline{MR}} = \sqrt{\sum_{i=1}^{m} k_i^2 S_{\overline{R}i}^2}, \tag{V}$$

where m is the number of bond types in the compound under study; k_i is the number of bonds of the given type; $\overline{R}_i$ is the most probable value of the refraction of a bond of the given type; $S_{\overline{R}i}^2$ is the variance of the quantity $\overline{R}_i$, characterizing the distribution of errors around the most probable value of the quantity $\overline{R}_i$; $S_{\overline{MR}}$ is the root-mean-square error of the most probable value of the calculated molecular refraction.

Then expression (I), for 100% probability, takes the form:

$$MR_{\text{calc}} = \sum_{i=1}^{m} k_i \overline{R}_i \pm 3\sqrt{\sum_{i=1}^{m} k_i^2 S_{Ri}^2} \tag{VI}$$

or

$$MR_{\text{calc}} = \overline{MR} \pm 3\sqrt{S_{MR}^2}. \tag{VII}$$

If an acceptable probability is taken to be 95%, then one may use the limits $2S$, i.e.:

$$MR_{\text{calc}} = \overline{MR} \pm 2\sqrt{S_{MR}^2}. \tag{VIIa}$$

Expression (VII) or (VIIa) is the basic expression by which $MR_{\text{calc,max}}$ and $MR_{\text{calc,min}}$ are calculated.

Table 1

Bond refractions and the corresponding variances

Bond or group type	Magnitude of the refraction of the bond or group	Variance S_{Ri}^2	Bond or group type	Magnitude of the refraction of the bond or group	Variance S_{Ri}^2
C—H	1.676	$0.197 \cdot 10^{-6}$	B—N	1.910	$0.137 \cdot 10^{-2}$
C_{al}—C_{al}	1.296	$0.982 \cdot 10^{-6}$	B—O	1.61	$0.082 \cdot 10^{-2}$
CH_2	4.643	$0.207 \cdot 10^{-6}$	B—C_{al}	1.93	$0.024 \cdot 10^{-2}$
C_{al}—N	1.583	$2.84 \cdot 10^{-4}$	B—Cl	6.88	$0.256 \cdot 10^{-2}$
N—H	1.764	$3.11 \cdot 10^{-4}$			

Table 1 gives the most probable values of bond refractions needed for the calculation and the corresponding variances. Since we were interested in organic boron compounds, and first of all boron-nitrogen compounds, only some of the most frequently used bond refractions have been included in the table.

We recalculated $R_{\text{C-C}}$ and $R_{\text{C-H}}$ in aliphatic hydrocarbons, using n_D^t and ρ_4^t from recent publications ([5,6]), and the results of the calculations agreed well with Denbigh' s data ([7]). Approximate calculations showed that in practical work one can successfully use the group refractions accepted in the literature (of alkyl groups), while calculating the variances, as usual, from the number of C—C and C—H bonds.

The values $R_{C_{al}-N}$ and R_{N-H}, and the corresponding variances, were calculated by us by the method of least squares, as recommended by Denbigh ([7]), on the basis of the data of Vogel and co-workers ([8]).

Such a solution, after exclusion of values burdened with gross measurement errors, gives $R_{C_{al}-N} = 1.583$ and $R_{N-H} = 1.764$, which differ little from Vogel' s data: 1.57 and 1.76, respectively. On the basis of the obtained

using these data, the refraction of the boron-nitrogen bond was calculated. This value was previously calculated by Mikhailov and co-workers ([1])—1.98, and by Seri ([2])—1.958.

In calculating the refraction of the boron-nitrogen bond, one must be very cautious in selecting the starting compounds. This is explained above all by the high hydrolyzability of most boron-nitrogen compounds, and in some cases also by great difficulties in obtaining analytically pure samples.

The value of the calculated quantity R_{B-N} depends not only on the purity of the products and, consequently, on the reliability of n_D^t and ρ_4^t, but also on the number of initial data, or, in other words, on the size of the sample by which the quantity of interest is determined. The larger the sample, the more accurately the value of R_{B-N} and its dispersion can be calculated. However, this requirement is difficult to fulfill, since at present a rather limited number of compounds of the type BX_n have been described. Moreover, even the described compounds cannot always be used, since their physical constants—the refractive index and density—sometimes raise doubts. Thus, for example, one has to discard the data for tris-(di-*n*-propylamino)-boron, methyl- and ethylamino-bis-(diisopropylamino)-boron. In the last two cases the calculation gives a negative value for the refraction of the B—N bond, which, of course, is unacceptable.

We calculated the value of R_{B-N} from the literature data for 13 trisamides of boric acid. It was found that the most probable value of this quantity is 1.910, and the dispersion, found from the formula:

$$S^2_{\overline{R}_{B-N}} = \frac{\sum_{i=1}^{n}(R_i - \overline{R})^2}{n(n-1)}, \qquad \text{(VIII)}$$

is equal to $0.137 \cdot 10^{-2}$. The dispersions of the refraction values of boron bonds with other elements, given in Table 1, were calculated in an analogous manner from the data of Mikhailov and co-workers ([1]).

In conclusion we shall give one example. The *n*-propylamino-bis-(diethylamino)-boron synthesized by us earlier ([9]) has $n_D^{20} = 1.4432$; $\rho_4^{20} = 0.8272$, $MR_{\text{exp}} = 68.44$. From the data of Table 1 we calculate: $\overline{MR} = 68.342$; $S^2_{\overline{MR}} = 2.078 \cdot 10^{-2}$. The maximum and minimum values of the calculated molecular refraction are respectively: (a) for the limits $3S$, 68.775 and 67.909; (b) for the limits $2S$, 68.630 and 68.054.

We consider it our pleasant duty to express our gratitude to A. A. Gundyrev for a useful discussion of the work.

Since

$$\underset{68.630}{MR_{\text{calc., max}}} > \underset{68.44}{MR_{\text{exp}}} > \underset{68.054}{MR_{\text{calc., min}}},$$

we may state that, judging by the molecular refraction, the structure of the compound obtained corresponds to the proposed structure of *n*-propylamino-bis-(diethylamino)-boron.

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Note: Figure translations are in progress. See original paper for figures.